Enumeration of Graphite Carbon-Bond-Network
Defects Having Ring Sizes Ranging from 2 to 9.

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Graphite-like Structures

A covering of the plane by congruent regular n-gons (all vertex angles and edge lengths are equal) is called a *regular* tessellation of the plane (1). The graphite σ-bond structure is a regular tessellation of the plane by hexagons. The only regular tessellations of the plane by n-gons are for n = 3,4, and 6; no other regular tessellations of the plane exist. If m denotes the number of regular n-gons at every vertex, then $m(1-2/n)\pi$ = 2π which simplifies to $1/n$ + $1/m$ = $\frac{1}{2}$. *Homogeneous* tessellations (all edge lengths are equal) occur when different polygons are used with the same set of polygons at each vertex. Since the number of n-gons at every vertex is three for the graphite σ-bond structure, the various isomeric graphite tessellations in a plane must be given by $(1-2/n_1)$ + $(1-2/n_2)$ + $(1-2/n_3)$ = 2 which simplifies to $1/n_1$ + $1/n_2$ + $1/n_3$ = $\frac{1}{2}$. The only acceptable solutions to the latter equation for n_1, n_2, n_3 are 6,6,6 or 3,12,12 or 4,6,12 or 4,8,8. These translate to the tessellated structures shown in Figure 1. Note that these tessellated graphite related structures are listed in decreasing order of their aromatic or pπ-bond energy stability associated with polycyclic conjugated hydrocarbons where the hexagonal web (n_1 = 6, n_2 = 6, n_3 = 6) is totally aromatic (n_1 = 3, n_2 = 12, n_3 = 12) or have aromatic and *antiaromatic* components (n_1 = 4, n_2 = 6, n_3 = 12), and the latter structure is almost totally antiaromatic (n_1 = 4, n_2 = 8, n_3 = 8). The homogeneous tessellated structures (Figure 1) have only angle distortions from the ideal angle of 120° for the graphite structure. If bond (edge) distortions are permitted then other planar lattice structures become possible (2). They include plane nets composed of an equal number of pentagonal and heptagonal rings or trigonal and nonagonal rings and twice the number of pentagonal rings to octagonal rings or twice the number of heptagonal rings to tetragonal rings in compliance with the equation $3r_3+2r_4+r_5-r_7-2r_8-3r_9-4r_{10}-5r_{11}-6r_{12}-\cdots$ = 0 (*vide infra*) where r_n is the number of rings of size n.

These other graphite lattices are unknown but can possibly exist as island defects in graphite or amorphous carbon (carbon-bond-network defects). Twinning of graphite crystals result in the formation of 4- and 8-membered rings along the twinning line. Similarly, a partial lateral dislocation leads to a similar 4-8 boundary. A single carbon-atom-lattice-vacancy forms a hole shaped like peri-naphthenyl radical and a two-carbon-atom-lattice-vacancy forms a hole shaped like pyrene (3). A partial line dislocation can produce a sp³-hybridization-buckled-network defect (4). Other types of graphite defect structures involve layer stacking and foreign atom incorporation. The 419 other isomers of pyrene enumerated in a previous paper also represent other possible carbon-bond-network defect structural units that may possibly exist as localized islands in graphite and amorphous carbon (5).

Diamond-like Structures

There are two basic three-dimensional 4-connected nets or lattices that can be constructed with equal links and regular tetrahedral bond angles (6). The most stable is the (cubic) diamond-like lattice which is made up of the totally staggered arrangement of links where each and every two-tetrahedral-atom unit resembles the staggered conformation of ethane and every six-tetrahedral-atom ring system resembles the chair conformation of cyclohexane. The less stable wurtzite-like (hexagonal diamond) lattice is composed of 1/4 eclipsing links and 3/4 staggered links and has (normal) layers of made up of fused polycyclic hexagonal rings in chair conformational-like arrangements which are mutually joined in such a way that boat conformational-like hexagonal rings are formed between these layers. A lattice which alternates in a regular or periodic manner between the cubic and hexagonal diamond structures could lead to the SiC polytypes. Two other lattices possible for 4-connected tetrahedral atoms are worthy of note (6). One is based on the cyclopentagon which has an internal angle of 108° that is close to the regular tetrahedral angle value of 109.5°. A net which radiates out from a central pentagonal dodecahedron can be constructed. The other is based on the planar (and angle strained) cyclohexagon. An infinite net which radiates from a column of planar cyclohexagons leads to a structure that can be described as a 6-fold rotation twin of cubic diamond.

Isomer Enumeration of Polycyclic Conjugated Hydrocarbons

Consider the σ-bond graphs of three of the 420 possible polycyclic conjugated hydrocarbon isomers of pyrene shown in Figure 2 (5). Pyrene (1) has $N_{p_c}=4$ peripheral third degree carbon vertices (numbered 1 to 4), isomer 2 has $N_{p_c}=5$, and isomer 3 has $N_{p_c}=6$; all pyrene polycyclic conjugated isomers have $N_H=10$ second degree vertices on the periphery of their σ-bond graphs. Note that the previously derived equation of $N_{p_c}-N_H+6=3r_3+2r_4+r_5-r_7-2r_8-3r_9-\cdots$ correctly enumerates the relative number of ring sizes different from the hexagonal ring in these three pyrene isomers (1 to 3).

Carbon-Bond-Network Defects in Graphite

The principle assumption in this treatment of carbon-bond-network defects is that this kind of defect is formed in an initially ideal graphite lattice in such a manner that the initial number of carbon atoms are conserved (i.e., Frenkel-like defects). Also, the graphite crystal is regarded basically as a super-large polycyclic aromatic hydrocarbon and that these carbon-bond-network defects occur remote to the crystal edge; under these conditions $N_{p_c}-N_H+6=q_p-2N_H+6=3r_3+2r_4+r_5-r_7-2r_8-3r_9=0$ since $N_{p_c}-N_H+6=0$ for benzenoid PAHs. A two-dimensional projection on the (1$\bar{1}$0) plane of the diamond lattice gives a 6-gon tessellated structure with hexagonal rings possessing two shortened parallel edges. Dislocations in the diamond lattice of silicon parallel to this (1$\bar{1}$0) plane result in ring size combinations which obey the above general equation as a consequence of avoiding energetically unfavorable dangling bonds (7). A (1$\bar{1}$0) projection of the diamond-cubic lattice of germanium containing an intrinsic Z-shaped faulted dipole was shown to exhibit a combination of pentagonal and heptagonal rings ($r_5-r_7=0$) which complies with the above equation (8). A study of <011> tilt boundaries in the diamond-cubic lattice gave a two-dimensional projection showing ring size combinations consistent with this equation (9).

Naphthalene has only four polycyclic conjugated hydrocarbon isomers as enumerated in Figure 3. If one takes an ideal graphite lattice, excises out a naphthalene substructure, and replaces it with a substructure corresponding to the other three naphthalene isomers, one obtains the three carbon-bond-network defects enumerated in Figure 4; the graphite partial structure shown in Figure 4 will be

referred to as the ovalene graphite cell. Similarly, if one excises out a
pyrene substructure from an ideal graphite lattice and replaces it with another
substructure corresponding to one of the other 419 isomers of pyrene, one obtains
other carbon-bond-network defects. Note that for all the defect graphite cell
structures shown in Figure 4, the combination of ring sizes is predicted by
$3r_3+2r_4+r_5-r_7-2r_8-3r_9=0$. If one distinguishes between rings of the naphthalene
the outer rings formed upon their insertion into the ovalene graphite cells, then
the equation $3r_3+4r_4+5r_5+6r_6+7r_7+8r_8+9r_9= q_p+2q_I$ can be partitioned into the two
following equations where the superscript "i" designates "inner" and the
superscript "o" designates "outer" ring system:

$$3r_3+4r_4+5r_5^i+6r_6^i+7r_7^i+8r_8^i+9r_9=q_p^i+2q_I^i$$

$$5r_5^o+6r_6^o+7r_7^o+8r_8^o=q_p^o+2q_I^o$$

These equations with specific values for q_I^i, q_p^i, q_I^o, q_p^o, and N_{Ic}^i are given in
Figure 4. If one excises the pyrene structural unit from the circumpyrene ideal
graphite cell, rotates the pyrene structural unit, and reinserts it, then one
obtains another carbon-bond-network defect. Thus there are probably more than
419 different elementary carbon-bond-network defects since each of the different
420 structural isomeric units of pyrene can be inserted with different orientations
into the empty circumpyrene graphite cell. The simplest carbon-bond-network
defect is that graphite cell corresponding to azupyrene since the surrounding
graphite hexagonal units would be nearly normal. Carbon-bond-network defects
having ring sizes 3 to 9 are shown to be most probable within the constraints
of this model.

A recent example of thermal (500°C) isomerization of azupyrene to pyrene
has been published (10). This example (Figure 5) is probably mechanistically
the simplest type of isomerization possible for pyrene isomers since a pairwise
detachment and reattachment exchange of *syn* internal bonds to the internal third
degree carbon atom vertices would convert azupyrene to pyrene. Annealing graphite
with analogous defects can cause their migration to the surface or annihilate
them as shown in Figure 5.

Although large vacancy defects no doubt exist in graphite, one or two carbon-
atom-lattice-vacancies most likely do not exist. Point defects have excess energy
due to strain and dangling bonds. Each dangling bond amount to ~2.5eV, and thus
there will be a tendency to form point defects which minimize the number of
dangling bonds. Consider a two carbon-atom-lattice-vacancy which forms a hole
which is shaped like pyrene (3); the four dangling bonds in this defect could
form two bridging bonds if some lattice distortion and associated strain energy
is permitted. Since it is likely that this strain energy is less than 10 eV, the
equilibrium in Figure 6 probably lies to the right side of the equation; note
that the equation $3r_3+2r_4+r_5-r_7-2r_8-3r_9=0$ is again obeyed (i.e., $r_5-2r_8=2-2x1=0$).

These examples demonstrate the broad applicability of the general equation
$3r_3+2r_4+r_5-r_7-2r_8-3r_9-\cdots=0$ for predicting the relative number of nonhexagonal ring
sizes in planar graphs of molecular carbon systems where minimization of dangling
bonds is a dominant energetic factor. Amorphous carbon can be regarded as a mix
of graphite and diamond lattice types and carbon-bond-network defects (11). These
structural concepts should be useful in study of the mechanism of carbonization by
which pitch is thermally converted to coke and coke to graphite (12).

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APPENDIX: Glossary of Terms

N_c - total number of carbon atoms in a PAH

N_H - total number of hydrogen atoms in a PAH

N_{Ic} - number of internal carbon atoms in a PAH having a degree of 3

N_{Pc} - number of peripheral carbon atoms in a PAH having a degree of 3

PAH6 - polycyclic aromatic hydrocarbon containing exclusively fused hexagonal rings

$|P|=p=Nc$ - total number of graph points

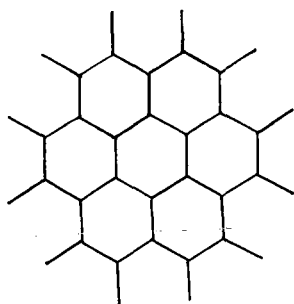P_3 - number of graph points (vertices) having a degree of 3

$|Q|=q$ - number of graph edges (lines or C-C bonds)

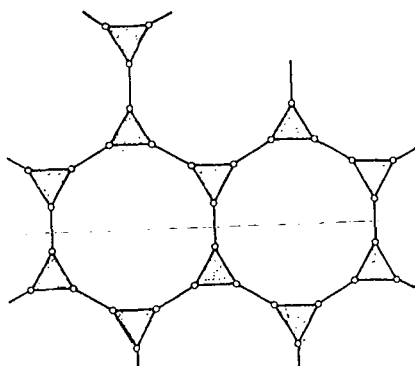q_I - number of internal graph edges

q_p - number of peripheral graph edges

q_b - number of graph edges connecting to phenyl-like ring substituents
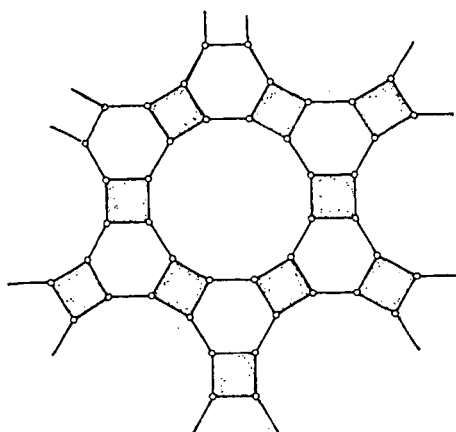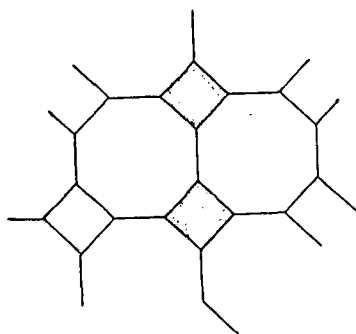
r - number of rings

$n_1 = 6, \; n_2 = 6, \; n_3 = 6$

$n_1 = 3, \; n_2 = 12, \; n_3 = 12$

$n_1 = 4, \; n_2 = 6, \; n_3 = 12$

$n_1 = 4, \; n_2 = 8, \; n_3 = 8$
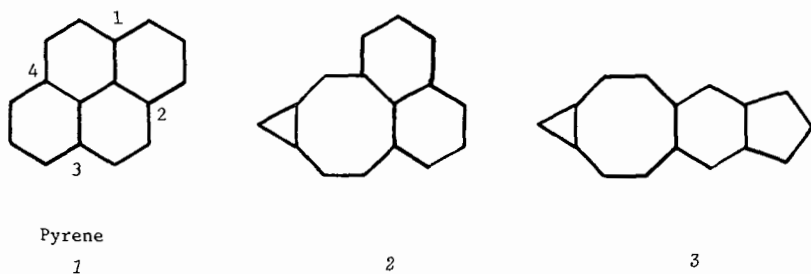
Figure 1 . Graphite related tessellated structures.

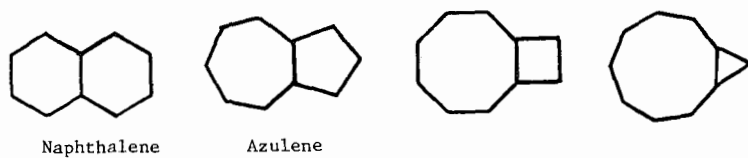Figure 2.   Three of the 420 possible polycyclic conjugated hydrocarbon isomers of pyrene.

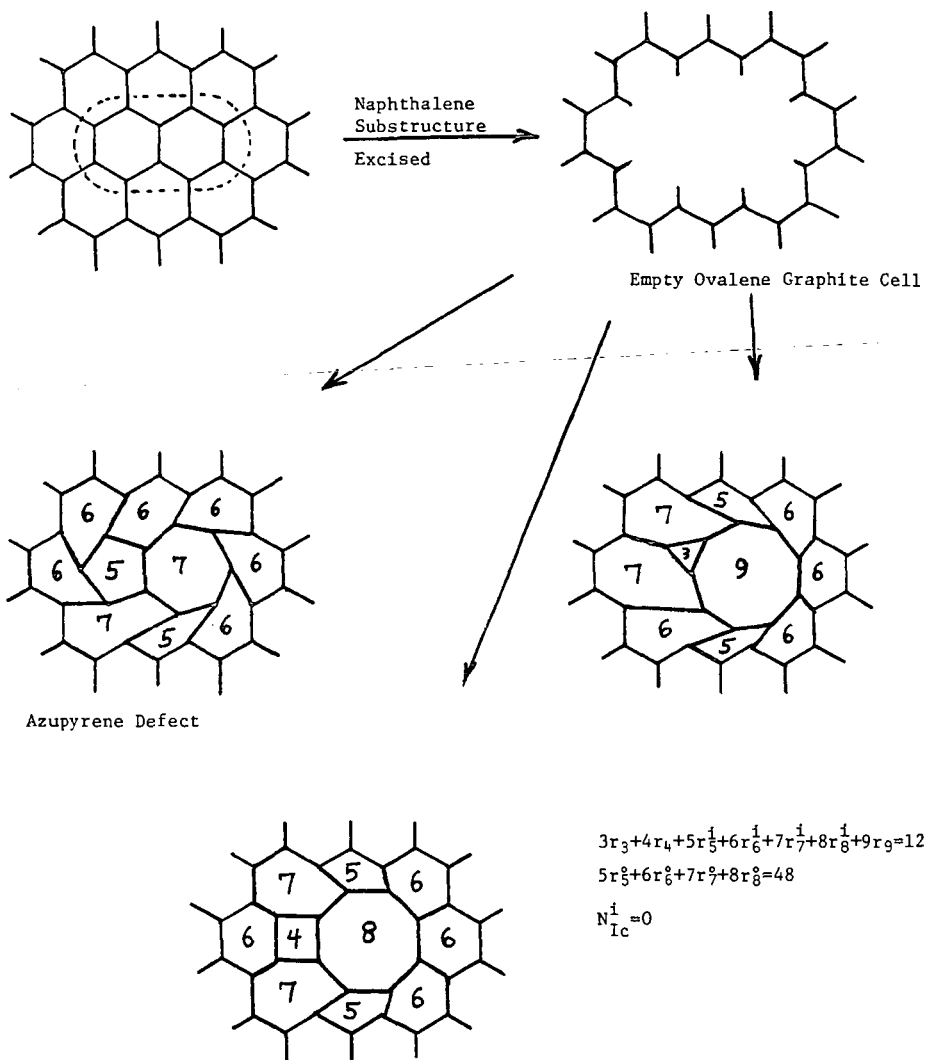Figure 3.   Polycyclic conjugated isomers of naphthalene.

$$3r_3+4r_4+5r_5^{\frac{1}{5}}+6r_6^{\frac{1}{6}}+7r_7^{\frac{1}{7}}+8r_8^{\frac{1}{8}}+9r_9=12$$

$$5r_5^o+6r_6^o+7r_7^o+8r_8^o=48$$

$$N_{Ic}^i=0$$

Figure 4. Carbon-bond-network defects in ovalene graphite cells.
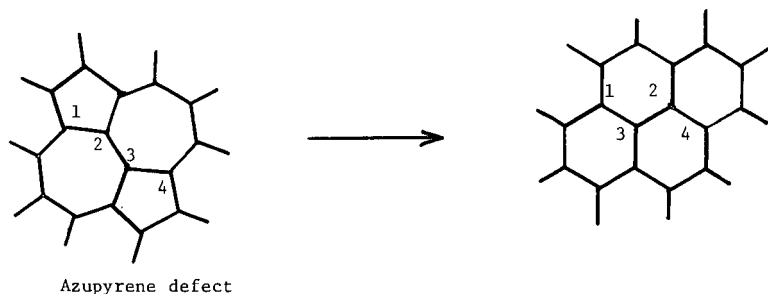
Azupyrene defect
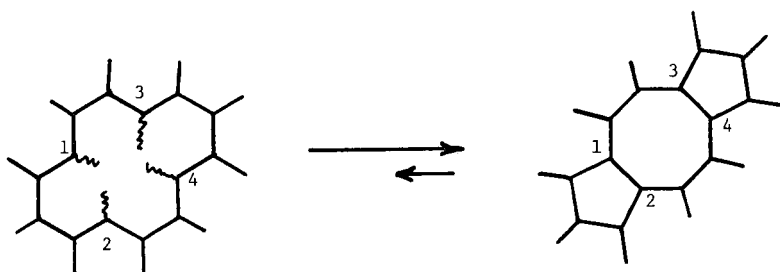
Figure 5. Thermal isomerization of azupyrene to pyrene.

Figure 6. Example of minimization of dangling bonds.